



# Optimization of Tapioca Oxidative Reaction by Ozone Treatment: Effect of pH, Process Time and Temperature

Siswo Sumardiono<sup>1</sup>, Isti Pudjihastuti<sup>2</sup>, Edy Supriyo<sup>2</sup> and Anggun Puspitarini Siswanto<sup>2\*</sup>

<sup>1</sup> Department of Chemical Engineering, Faculty of Engineering, Diponegoro University

<sup>2</sup> Department of Industrial Chemical Engineering, Vocational School, Diponegoro University

e-mail: [anggun.siswanto@live.undip.ac.id](mailto:anggun.siswanto@live.undip.ac.id)

**Abstract-** Modification of cassava starch was produced by oxidation using ozone treatment. The oxidized starch is used in the paper processing in the pulp and paper industries. The aim of this research was to determine the effect of reaction conditions (pH and temperature) in produced oxidized starch. The oxidative reaction of cassava starch was using ozone as an oxidator while the operating condition was at temperatures of 30, 35, 40 and 45 °C in atmospheric pressure. The fixed variables were weight of cassava starch 80 grams, and volume of aquadest 200 ml. The change variables are reaction time (15, 30, 45 and 60 minutes) and pH solution (6, 7, 8 and 9). The product of oxidized starch was analyzed for carboxyl group according to JEFA method, swelling power according to Leach method and solubility according to Kainuma method. The result of this research shows with an increasing of pH reaction and reaction time, the carboxyl group and solubility increased, but swelling power decreased. The best condition was obtained at the pH of 9 with 60 minutes of reaction time.

**Keywords** - carboxyl group; cassava starch; oxidation; solubility; swelling power

Submission: February 29, 2020

Correction: May 05, 2020

Accepted: May 11, 2020

Doi: <http://dx.doi.org/10.14710/jvsar.2.1.2020.1-6>

[How to cite this article: Sumardiono, S., Pudjihastuti, I., Supriyo E., and Siswanto A.P. (2020). Optimisation of Tapioca Oxidative Reaction by Ozone Treatment: Effect of Ph, Process Time and Temperature. *Journal of Vocational Studies on Applied Research*, 2(1), 1-6. doi: <http://dx.doi.org/10.14710/jvsar.2.1.2020.1-6>]

## 1. Introduction

Starch plays an important role in the food processing industry. Starch is widely used in industries such as paper, glue, textiles, candy, glucose, dextrose, fructose syrup, and others. In trade, there are two types of starches, namely Native Starch and Modified Starch [1, 2]. Natural starches such as tapioca, corn starch, sago and other starches have several obstacles if used as raw materials in the food and non-food industries. If cooked starch requires a long time, also the paste is formed hard and not clear. Besides that, it is too sticky and cannot stand acid treatment. These constraints cause limited use of natural starch in the industry.

The main sources of starch in Indonesia include: rice, corn, potatoes, tapioca, sago, wheat and others [3]. In a pure state, starch granules are white, shiny, odorless and tasteless, wherein microscopically starch granules are formed by molecules that form thin layers that are arranged centrally [4]. Starch granules vary in shape and

size, where there are round, oval, or irregular shapes. Likewise, in size, ranging from less than 1 micron to 150 microns, this depends on the source of the starch.

### 1.1. Starch Granules

Starch in plant tissue has different granular forms. Microscopic appearance of starch granules such as shape, size, uniformity, is typical for each type of starch. The physical form of starch granules is semi crystalline consisting of crystalline units and amorphous units. Crystal Units are more resistant to the treatment of strong acids and enzymes. Amorphous parts can absorb cold water up to 30% without damaging the overall starch structure.

Starches derived from certain grains contain only amylopectin, known as "waxy" or wax. Important species are sorghum wax, corn wax and rice wax.

### 1.2. Amylose

Starch is a glucose carbohydrate polymer and consists of amylose and amylopectin. Amylose is a polymer part with  $\alpha$ - (1,4) bonds from glucose units forming a straight

chain and is generally said to be linear from starch [5]. The characteristic of amylose in a solution is the tendency to form very long and flexible coils that always move in a circle. This structure underlies the interaction of iodamyllose to form blue. In cooking, amylose has a hard effect on starch or flour [5]. The structure of amylose chains tends to form linear chains.

### **1.3. Amylopectin**

Amylopectin such as amylose also has  $\alpha$ - (1,4) bonds in its straight chain, and  $\beta$ - (1,6) bonds at its branching point. The structure of amylopectin chains tends to form branched chains. Branching bonds amount to about 4-5% of all bonds in amylopectin. Amylopectin usually contains 1000 or more units of glucose molecules for each chain. The molecular weight of glucose amylopectin for each chain varies depending on the source. Amylopectin in tubers starch contains small amounts of phosphate esters that are bound to the 6th carbon atom of the glucose ring [4].

Amylopectin and amylose have different physical properties. Amylose is more soluble in water than amylopectin. If amylose is reacted with an iodine solution it will form a dark blue colour, while amylopectin will form a red colour. In food products, amylopectin is stimulating the process of blooming (puffing) in which food products derived from starch which have high amylopectin content will be mild, porous, crisp and crunchy. In contrast, starch with high amylose content tends to produce a hard, solid product, because the blooming process is limited [5].

### **1.4. Starch Modification Process**

Modified starches are starches whose hydroxyl groups have been altered by a chemical reaction (esterification or oxidation) or by disturbing the original structure. Starch is given a certain treatment in order to produce better properties to improve the previous properties or to change some of the previous properties or to change some other properties. This treatment can include the use of heat, acids, alkalis, oxidizing agents or other chemicals that will produce new chemical groups and or change the shape, size and structure of starch molecules [3, 4].

Modification of starch by oxidation has been widely carried out by previous researchers, especially the most popular ones, namely hypochlorite oxidation including: [6] investigating the effect of adding hypochlorite concentrations to different starch in hypochlorite oxidation. [1] investigated the modification of hypochlorite starch oxidation with varying reaction conditions at pH 7-11 and reaction time of 30-300 minutes. [7] studied the structure, morphology and psychochemistry of oxidation of wheat starch and compared with corn starch. Oxidation with hypochlorite has several disadvantages, including: producing residues and forming chlorine compounds during the reaction.

This research will apply ozone as an oxidizer in food products. Ozone oxidation is the process of adding O atoms to OH groups in starches to form chains that tend to be longer and can change the psychochemical properties of starch. The remaining O<sub>2</sub> formed will be released into the

air. Research on ozone oxidation has been studied by previous researchers, namely [5] studying the effect of ozone and the addition of amino acids on the nature of rice starch. In this experiment, the ozonation time is 15 and 30 minutes and uses 3 types of amino acids, namely lysine, aspartic acid, and leucine. From these experiments ozonation was obtained within 30 minutes and using the addition of lysine (6%) will increase swelling power and viscosity. Based on the nature of ozone which is a strong oxidizer and dissolves within  $\pm$  23 minutes, the ozone is expected to be able to change the structure, the psychochemical and rheological properties of starch and produce non-residuals [5]. The basic problem of this research is to determine the effect of pH and temperature during the oxidation reaction, and to examine the psychochemical and rheological properties of the modified starch.

### **1.5. Psychochemical and Rheology of Modified Tapioca**

Modified starches are starches whose hydroxyl groups have been altered by a chemical reaction (esterification or oxidation) or by disturbing the original structure. Starch is given a certain treatment in order to produce better properties to improve the previous properties or to change some of the previous properties or to change some other properties. This treatment can include the use of heat, acids, alkalis, oxidizing agents or other chemicals that will produce new chemical groups and change the shape, size and structure of starch molecules [3].

Some methods that can modify starch include modification by plant breeding, conversion by hydrolysis, cross linking, chemical derivatization, turning into syrup and sugar and changing physical properties. Modification by conversion is intended to reduce the viscosity of raw starch to be cooked and used at higher concentrations, starch will be more soluble in cold water and improve the nature of the tendency of starch to form a gel or paste [3].

The psychochemical properties of starch are those that show the morphology, structure, and crystallinity of starch. These properties will affect the starch granules in the form of gels, solutions, and crystals. Amylose and amylopectin content have a very big influence on the physical properties of starch. Both are interrelated in changing or forming different characteristics depending on the treatment. In this case including the psychochemical properties of starch include amylose and amylopectin content, viscosity, gelatinization, and swelling power [7].

The psychochemical and rheological properties of modified tapioca products such as swelling power, solubility, carbonyl groups and carboxyl groups have certain standards based on previous research, as seen in Table 1. Sealing power is the strength of flour to expand, swelling power is weight ratio of pasta with the weight of dry starch, this paste includes amylopectin which is insoluble in water [5]. Factors that influence include: amylose-amylopectin ratio, chain length and molecular weight distribution. Tapioca flour has medium swelling power compared to potato starch and cereal.

Table 1. Standard of tapioca psychochemical and rheology properties

Psychochemical	Value
Swelling power (g/g)	18,16
Solubility (%)	2,23
Carbonyl (%)	0,03
Carboxyl (%)	0,07
Viscosity (cp)	5107,7

## 2. Methods

### 2.1 Materials

The main ingredient in this research is bulk tapioca flour which is an artificial product from Lampung and aquadest as a solvent. Other research materials include: NaOH p.a (Merck) and H<sub>2</sub>SO<sub>4</sub> p.a (Merck).

### 2.2 Apparatus

The main tool of this research is the ozonator which is equipped with a stirred tank reactor with a stirring speed of 54 rpm and a pump. Meanwhile other tools used include: oven, centrifuge, filter device, viscosimeter VT-04F spindle No 4, digital scales and pH meter.

### 2.3 Experimental Procedures

At this stage, it starts with dissolving tapioca in aquadest with a consistency of 10-40% (gr / 100 ml aquadest) and is put in a stirred tank reactor. Ozone gas is then flowed into the reactor with a time variation of 15, 30, 45 and 60 minutes. During the experiment the pH will be varied at 6, 7, 8 and 9 with accuracy  $\pm 0,1$  and the temperature of the solution is 30, 35, 40 and 45 °C. The pH of the solution is adjusted by the addition of NaOH or by H<sub>2</sub>SO<sub>4</sub>. Temperature regulation is carried out by dipping the stirred tank in the water bath. The modified starch product was then analysed to determine the physical characteristics of the starch which included: swelling power [8], solubility [9] and viscosity

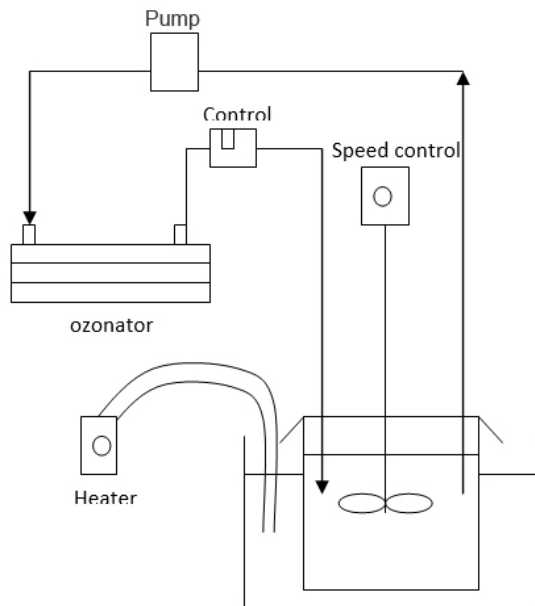


Figure 1. Experimental Set up

## 3. Results and Discussions

### 3.1 Effect of pH vs swelling power

The ozone oxidation process of starch was carried out at an ozone flow rate of 1.1584 gr / min with varied reaction pH of 6,7,8 and 9 in a constant consistency of 20% and fixed operating conditions for 30 minutes ozonation time and 30 °C temperature. each treatment then analysed its swelling power.

Figure 2. Effect of pH vs swelling power

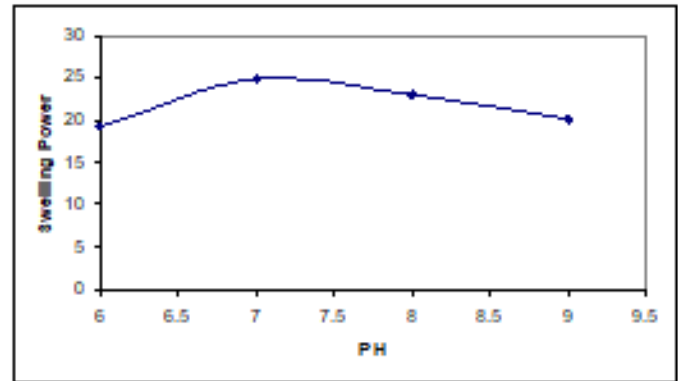


Figure 2 shows the relationship between pH and swelling power. Starch degradation is very easy to occur at a neutral pH compared to an alkaline pH of 9 or more. Starch will be degraded so that the amylose group will decrease so that it will tend to increase the paste [10]. Swelling power is a comparison of the weight of pasta with the weight of dry starch, this paste includes amylopectin which is not soluble in water. Therefore, if the content of amylopectin (pasta) is greater, the swelling power will also increase. It is shown in Figure 2 that the optimum pH is pH 7 with a swelling power of 24,881.

The effect of pH on starch is in the addition of carboxyl groups (C-O) and carbonyl groups (C-O-O-H). Both groups are very influential on the viscosity of the paste formed. Carboxyl is easily formed at a pH of more than 8.5, while carbonyl is formed at a pH range of 7-7.5. Depolymerization of starch occurs at pH 7, given the nature of amylose which is easily depolymerized compared to amylopectin so that at pH 7 the amylose chain is depolymerized and causes more paste to form [10]. More and more amylose is degraded resulting in decreased solubility of starch because the nature of the amylose which tends to dissolve in water decreases.

The swelling power value in Figure 2 shows a declining value, respectively from pH 6,7,8 and 9, namely 19,318; 24,881; 23,008; and 20,176. carboxyl is formed at a pH of more than 8.5, the presence of these groups can prevent amylose from being degraded. At pH 9 the swelling power decreases due to the amylose group formed so it tends to dissolve in water and cause a reduction in the paste formed.

At the pH of 6 where depolymerization has not yet occurred and a new carbonyl group has begun to form, so the formation of the paste has not been optimal. The

carbonyl group is very influential in the amylose degradation process, so that the amylose degradation increases the less amount of paste formed and will reduce the value of swelling power.

### 3.2 Effect of pH vs starch solubility

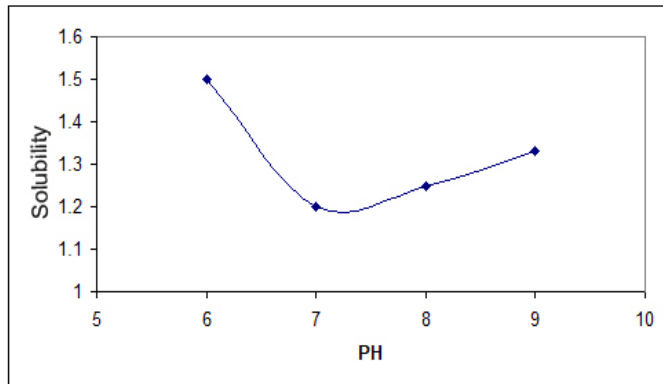


Figure 3. Effect of pH vs solubility

The effect of pH on starch is in the addition of carboxyl groups (C-O) and carbonyl groups (C-O-O-H). Both groups are very influential on the viscosity of the paste formed. Carboxyl is easily formed at a pH of more than 8.5, while carbonyl is formed at a pH range of 7-7.5. The existence of these carboxyl groups can prevent amylose from being degraded.

Starch depolymerisation occurs at pH 7, given the nature of amylose which is more easily depolymerized than amylopectin, causing more paste to form [10]. The presence of this paste shows that the solubility of the pasta decreases.

From Figure 3 the tendency of the higher pH will decrease the solubility. Consecutive solubility values for pH 6,7,8 and 9, namely 1,50; 1,20; 1,25; and 1.33. At pH 6 it has the highest solubility due to the fact that at that time depolymerization did not occur. The amylose group is most easily depolymerized compared to amylopectin, so that at pH 6 the solubility tends to be high because the amylopectin content is still high. As for pH 8 and 9, its solubility is increasing. In these circumstances the carboxyl group begins to form thereby preventing amylose from being degraded. Amylose has soluble properties in solution. This causes the starch solubility to increase.

### 3.3. Effect of temperature vs swelling power

The ozone oxidation process of starch was carried out at an ozone flow rate of 1.1584 gr / min with reaction temperatures varying at 30, 35, 40 and 45 °C in a constant consistency of 20% and fixed operating conditions for 30 minutes ozonation time and reaction pH 7. Each treatment is then analysed for swelling power. In Figure 4 shows the relationship between temperature and swelling power. The more the temperature increases, the swelling power will decrease. The higher the temperature, the starch granules will swell and will undergo depolymerisation resulting in

weak structure of the granules so that the swelling power will decrease [7].

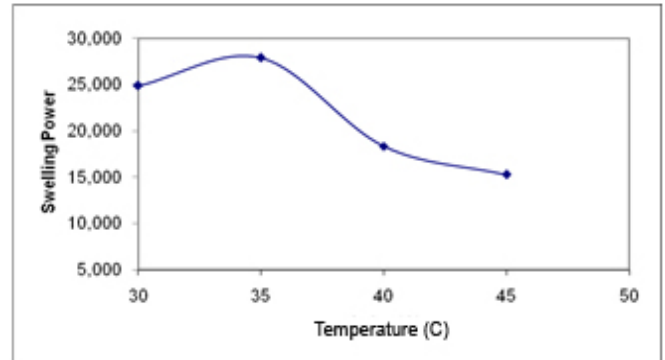


Figure 4. Effect of temperature vs swelling power

The oxidation process takes place before the gelatinization temperature is 50-67°C. This is because if a paste has formed then the process of dissolving ozone into the starch solution will be hampered so that the ozonation process runs imperfectly. This is indicated by the increasing temperature; the swelling power also decreases. In Figure 4 it can be seen that at a temperature of 35 °C an increase in swelling power of 27,891 because at that time the starch has not experienced gelatinization so that it can develop optimally. But after that at a temperature of 40 and 45 °C has decreased, here the gelatinization process has begun to occur so that ozone that is diffused into the starch granules becomes reduced ozone is not completely dissolved and causes the amylose chain to not be fully reduced. This causes the tendency of the granules to absorb water and expand to vary, some are large because the amylose chain has been reduced, and there is also a tendency to be small because the amylose chain has not been reduced so that the starch granules tend to absorb less water.

The effect of temperature in the oxidation process is on the gelatinization process. When starch gelatinized, the granules of starch granules develop optimally. The process of developing starch granules is due to the amount of water absorbed into each starch granule. The expanded starch granules cause swelling power to increase. But if this lasts longer with increasing temperature, then the starch granules that expand will be damaged longer. This will make it difficult for the starch granules to re-expand because of the reduced ability to absorb water. This will affect the swelling power which will decrease as shown in Figure 4.

### 3.4. Effect of temperature vs solubility

Figure 5 shows the relationship between temperature and solubility. Temperature is very influential on the solubility process. The higher the temperature, the solubility will also increase. In the starch oxidation process the temperature affects the starch granules. The increase in temperature causes an increase in the speed of the oxidation reaction. As the oxidation reaction increases, the

amount of degraded starch granules becomes smaller and increases water solubility [7].

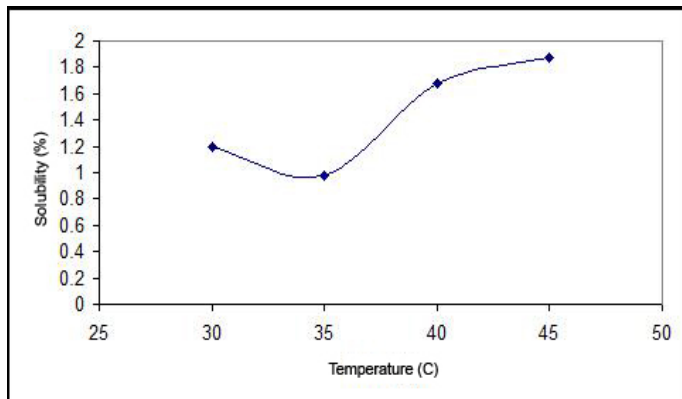


Figure 5. Effect of temperature vs solubility

Based on Figure 5 shows the tendency of solubility is increasing. The amount of solubility respectively 1.20, 0.98, 1.68 and 1.87. This increased solubility is due to the degraded granules getting bigger and forming the smallest parts so they are easily dissolved in water. During the oxidation process, there will be a chain breakdown of both amylose and amylopectin, and changes in the physical properties of starch. This breaking of the chain causes the starch granules to become smaller and easily dissolve in water. The longer the oxidation time, the shorter the chain so that the solubility will be even greater.

### 3.5. Effect of reaction time vs Carboxyl Concentration

The relationship between reaction time and carboxyl content (Fig. 6) shows that the longer the reaction time, the carboxyl content tends to increase. This is due to the increasing number of carboxyl which infiltrate the starch chain. The presence of these carboxyl groups precludes the reduction of amylose and retrogradation. From the graph, it can be seen that the highest amount of carboxyl content was obtained at pH 9, 0.93%. This is in accordance with JECFA requirements that the maximum carboxyl content obtained from the oxidation process is no more than 1.1%.

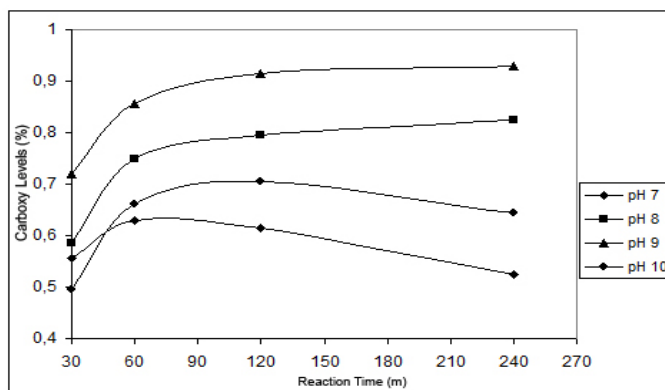


Figure 6. Effect of reaction time vs carboxyl concentration

### 3.9. Product Analysis

### 3.7. Effect of reaction time vs swelling power

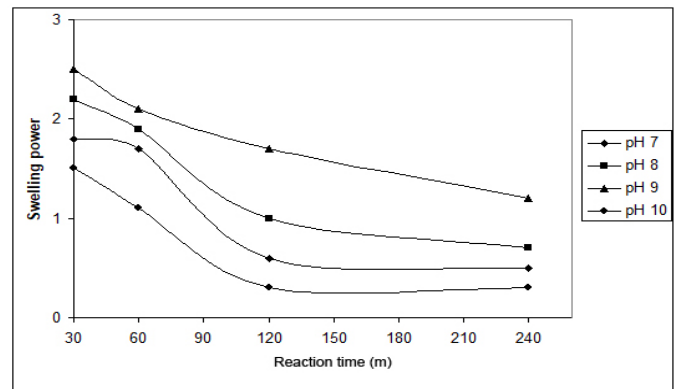


Figure 7. Effect of reaction time vs swelling power

From the graphic analysis results show that swelling power decreases with increasing reaction time. This is because of the increasing amount of amylose content. Starch with high amylose will prevent swelling, so the higher the amylose, the lower the swelling. The amylose in the oxidized modified starch will increase as the reaction time increases and as the carboxylic group contents increase.

### 3.8. Effect of reaction time vs solubility

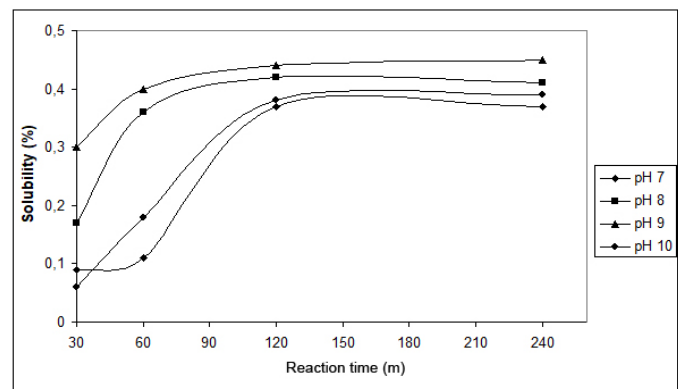


Figure 8. Effect of reaction time vs solubility

Solubility in oxidized starch increases with increasing reaction time. This increase in solubility indicates that oxidized modified starches dissolve easily in water, due to having granules with small size and high amylose content. Amylose in starch is more soluble in water than amylopectin. Based on the analysis that has been done shows that the best operating conditions for ozone oxidized modified starch is at pH 9 with a reaction time of 60 minutes. Because at the reaction time of 60 minutes an increase in carboxylic groups and solubility is the greatest of the other reaction times.



From the experimental results obtained optimum conditions of starch oxidized with ozone as well as before undergoing modification as seen in Tables 2 and 3.

Table 2. Optimum Condition of Modified Starch by Ozone Oxidation

Consistency (%)	Time (minutes)	pH	Temperature (°C)	Swelling Power	Solubility (%)	Viscosity (Cp)
20	30	7	35	24,18	2,204	1550
				29,38	2,386	1420
				24,30	2,534	1444
<b>Average</b>				<b>25,95</b>	<b>2,295</b>	<b>1471</b>

Table 3. Properties of native starch (before modification)

Swelling power	Solubility (%)	Viscosity (cp)
18,257	2,246	5107,7

From the above data it can be seen the difference between starch before modification and starch after modification. From the properties obtained, the modified starch has better properties than the native starch [11]. This is indicated by the increasing value of swelling power and solubility, as well as decreased viscosity. This corresponds to the literature regarding modification of starch hydroxypropylation. If the starch is made into noodle products, the power of blooming or expanding will increase so that it will form noodles with a crisper and softer texture. This is because high swelling power can increase amylopectin in starch. In food products, amylopectin is stimulating the process of blooming (puffing) in which food products derived from starch which have high amylopectin content will be mild, porous, crisp, and crunchy.

#### 4. Conclusion

Ozone oxidation is the process of adding O atom groups to OH groups in starches to form chains that tend to be longer and can change the physicochemical properties of starch. The results of the study found the influence of pH and temperature during oxidation. This can be seen from the increasing value of swelling power and decreasing viscosity of starch.

#### 5. Acknowledgment

We acknowledge DRPM for funding via Hibah Strategis Nasional Scheme.

#### 6. References

- [1] Sangseethong, K., Lertphanich, S., and Sriroth, K., 2009, Physicochemical Properties of Oxidized Cassava Starch Prepared under Various Alkalinity Level, *Starch/Stärke* Vol 61, 371-384.
- [2] Tonukari, J.N., 2004. Cassava and Future of Starch. *Electronic Journal of Biotechnology*. ISSN: 0717-3458, Vol 7 No 1. Issue of April 15, 2004
- [3] Tharanathan, Rudrapatnam, 2005, Starch- Value Addition by Modification, *Critical Reviews in Food Science and Nutrition*, Vol 45, 371-384.
- [4] Koswara, 2006, *Teknologi Modifikasi Pati*. Ebook Pangan.
- [5] Young An, 2005. Effects of Ozonation and Addition of Amino Acids on Properties of Rice Starches. A Dissertation Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College. Page. 38

- [6] Kuakpetoon, D., and Wang Y.J., 2001, Characterization of Different Starches Oxidized by Hypochlorite, *Starch/Stärke* Vol 53, 211-218
- [7] Murillo, C.E.C., Wang, Y.J., and Perez, L.A., 2008, Morphological, Physicochemical and Structural Characteristics of Oxidized Barley and Corn Starches, *Starch/Stärke* Vol. 60, 634-645
- [8] Leach, H W, McCowen LD, Schoch TJ., 1959. Structure of the starch granules in: swelling and solubility patterns of various starches. *Cereal Chem.* 36:534-544
- [9] Kainuma K, Odat T, Cuzuki S., 1967. Study of Starch phosphates monoesters. *J. Technology, Soc. Starch* 14:24-28.
- [10] Kesselmans. Annen. Ido Pleter Blecker. And ten Boer. 2004. Oxidation of Starch, United States Patent no 6.777.548.B1, 23 November 2004.
- [11] Narkrugs. Wand Emmerich Berghofer, 2000. Physicochemical Properties of Modified Cassava Flour and Starch for Carrugated Carrugated Board Adhesive. Bangkok Thailand